Analysis of Metals in Soils from Small Arms Ranges Using Incremental Sampling

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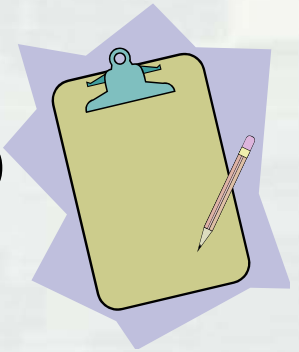
Feedback for 2010 EDQM Workshop



- More focus on case studies… Less theory...
- There seemed to be a lot more…statistics…Too much theory…
- Similar comments for 2009 Workshop

  … Thomas Georgian - great presenter! ALMOST made me want to be a statistician, then I regained my senses.

Warning !

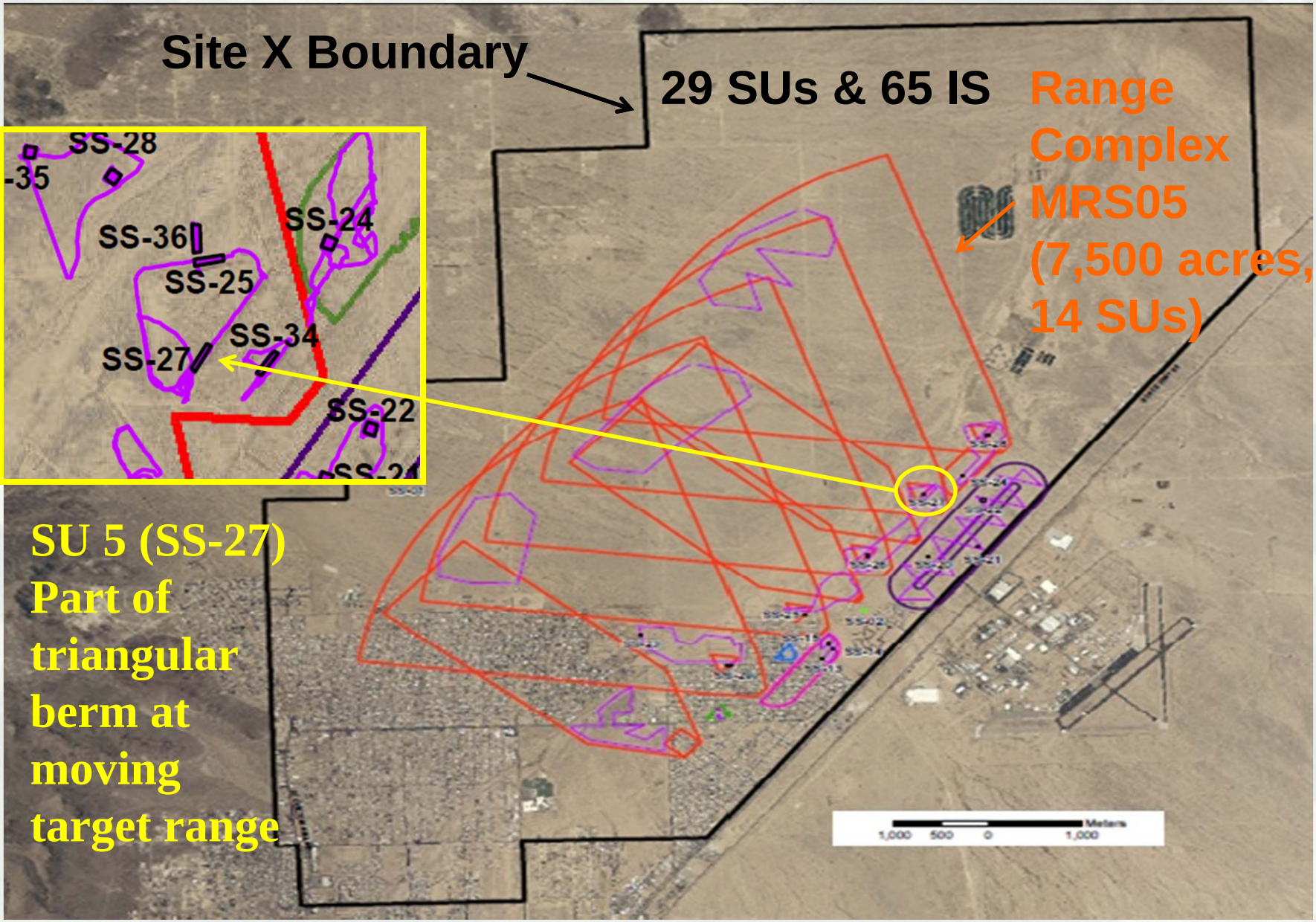
The following presentation contains information of a factual nature and mature technical content that may not be suitable for all audiences. If you are easily disturbed by use of strong scientific language, excessive mathematics, or graphic uncensored data of an explicitly statistical nature, viewer discretion is strongly advised.

PG

Probabilistic evaluations and **G**y's sampling theory used extensively.

Case Study Site Investigation (SI) of "Site X"

- 20,000-acre site with multiple skeet & small arms ranges.
- Stratified into ¼-acre Sampling Units (SUs) with highest suspected levels of contamination.
- 2-kg incremental samples (IS) of 100 increments from surface soils (0 – 2 inches) tested for metals (e.g., Cu, Pb, Zn & Sb) by Method 6010B, as well as PAHs by 8270C-SIM and explosives by 8330B.
- Splits of unground & ground lab sub-samples (steel puck mill in Method 8330B) analyzed.


Site X Boundary
29 SUs & 65 IS
Range Complex MRS05 (7,500 acres, 14 SUs)
SS-28
-35
SS-36
SS-25
SS-24
SS-34
SS-27
SS-22
SU 5 (SS-27) Part of triangular berm at moving target range
Meters
1,000 500 0 1,000

Replicate IS Samples (Unground) from SU with Small Arms Berm

Metal	IS Field Replicates (mg/kg) n = 7 (MRS05, SU#5)							Mean (mg/kg)	%RSD
Pb	170	200	**660**	240	160	130	380	**277**	**68%**
Cu	40	50	51	72	31	34	53	47	29%

Pb Screening Limit (SL) = 400 mg/kg.

Pb Concentrations (x) ≈ 100 – 700 mg/kg.

%RSD > 30% → Distribution not normal (but lognormal)

Are data usable to determine if site is "clean" or "dirty"?

Evaluating RSDs > 30%

- Work Plan:

  Provided…the calculated RSD is lower than the stated RSD [< 20 for lab triplicates, < 30 for field replicates]… the samples…can be reasonably assumed to be representative of the site conditions…

- Post-sampling: %RSD = 100% - 200% for replicates.

  Excerpt from contractor's tech memo: Whether [large %RSDs are] …appropriate…depends on…how close to a decision limit a concentration result might be. **It does not mean…data should be automatically rejected if the %RSD is greater [than 30%].**

I'm OK; you're OK,
even though your %RSDs are not OK.

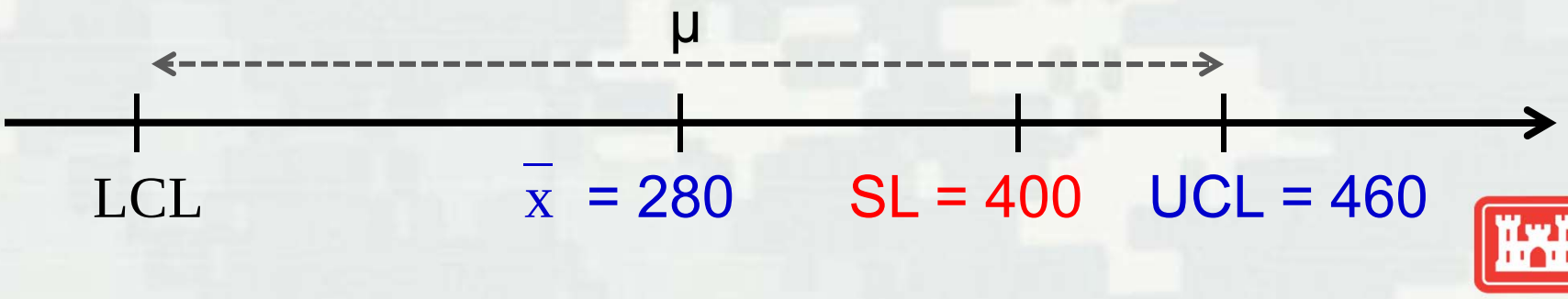
Technical Project Planning (TPP)

- 7-Step DQO Process implemented.
  - ► H_0: μ ≥ Screening Level (SL)

    Reject H_0 (i.e., conclude SU "clean") if 95% UCL < SL.

    Large variability (e.g., %RSD) increases UCL; RI needed if $\bar{x}$ < SL< UCL to determine if the site is "dirty."

    Example: Pb for MRS05, SU5 - Is site "dirty" or "clean"?



Laboratory IS Sub-samples

Metal	IS Field Replicates (mg/kg) *n* = 7 (MRS05, SU#5)							Mean (mg/kg)	%RSD
Pb	170	200	**660**	240	160	130	380	**277**	**68%**
Cu	40	50	51	72	31	34	53	47	29%

Sample used to prepare lab triplicates

Sub-sampling (within-sample) Variability

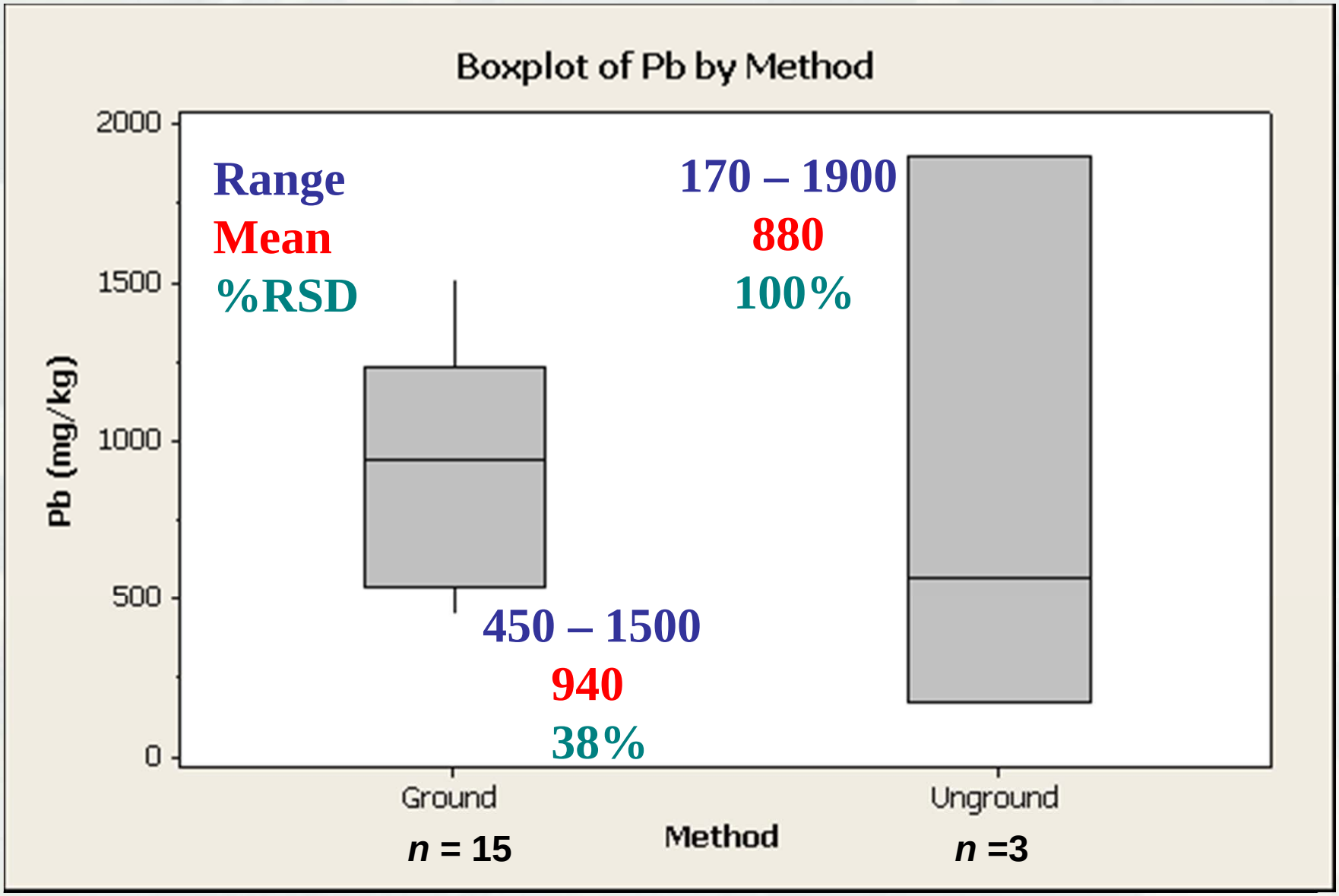
Metal	Laboratory Triplicate Sub-samples 1st Field Replicate (mg/kg)			Mean (mg/kg)	%RSD
Pb	170	**1,900**	**570**	**880**	**103**
Cu	40	46	59	48	12

Results not quantitatively reliable;
Pb varies by order of magnitude within single sample !

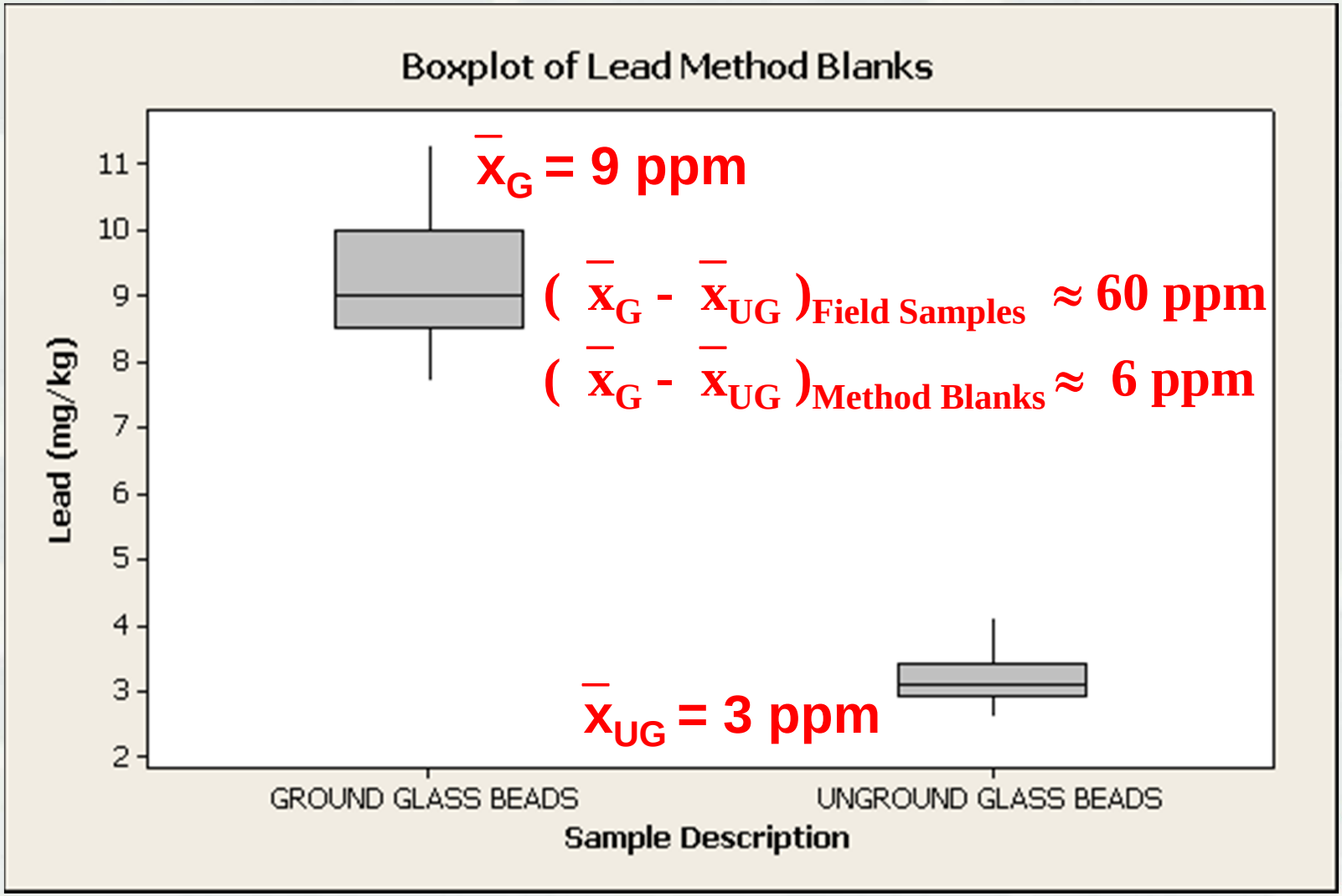
$\sigma_{Total} \approx 190$ ppm (Total variability, $n = 7$)
$< \sigma_{Lab} \approx 940$ ppm (Lab sub-sampling variability, $n = 3$) **!**

- σ_{Total} biased low; $n = 7$ unground field replicates too small to reliably estimate σ_{Total} and do statistical evaluations.

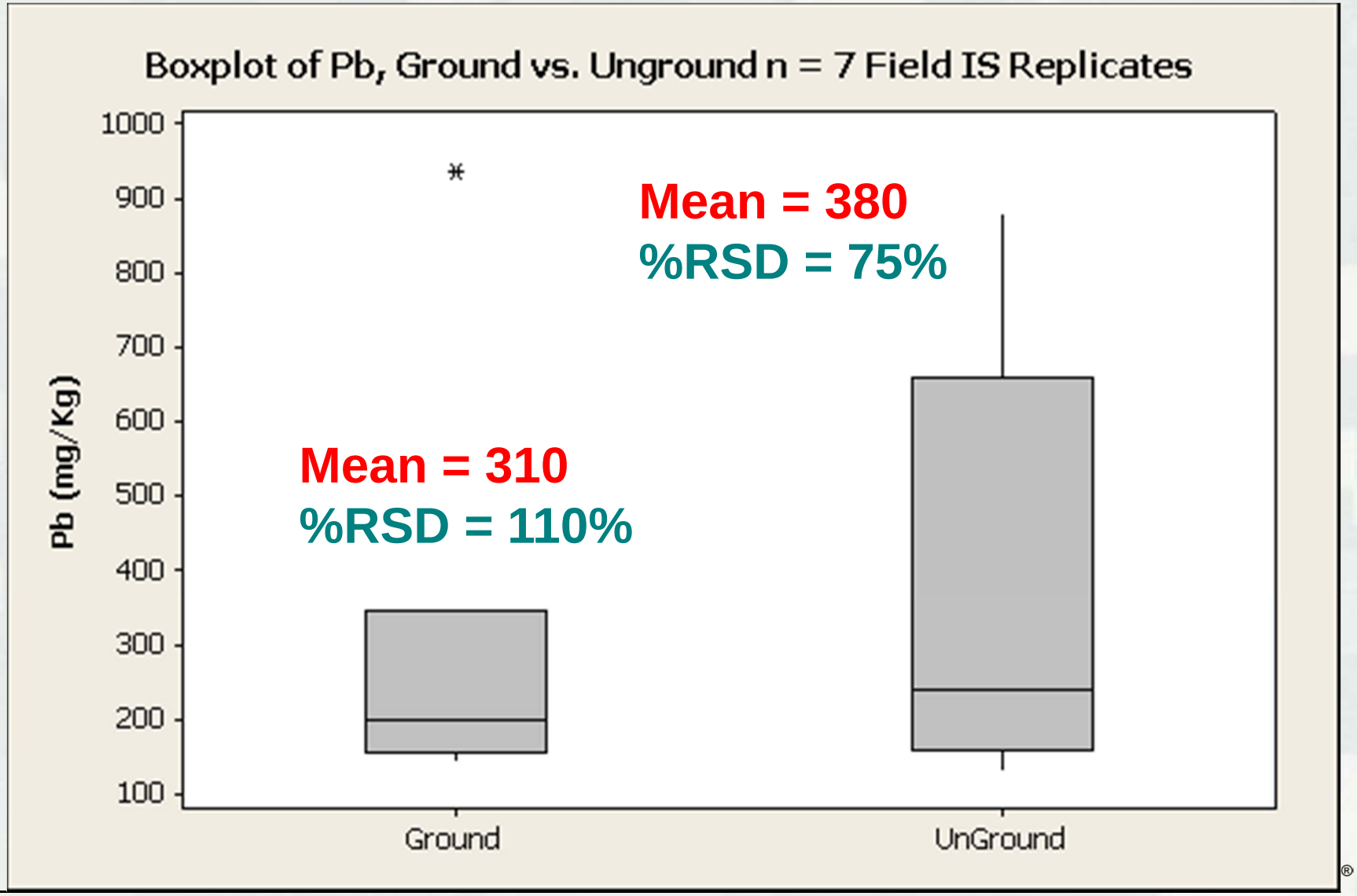
Ground vs. Unground Pb (Same IS)

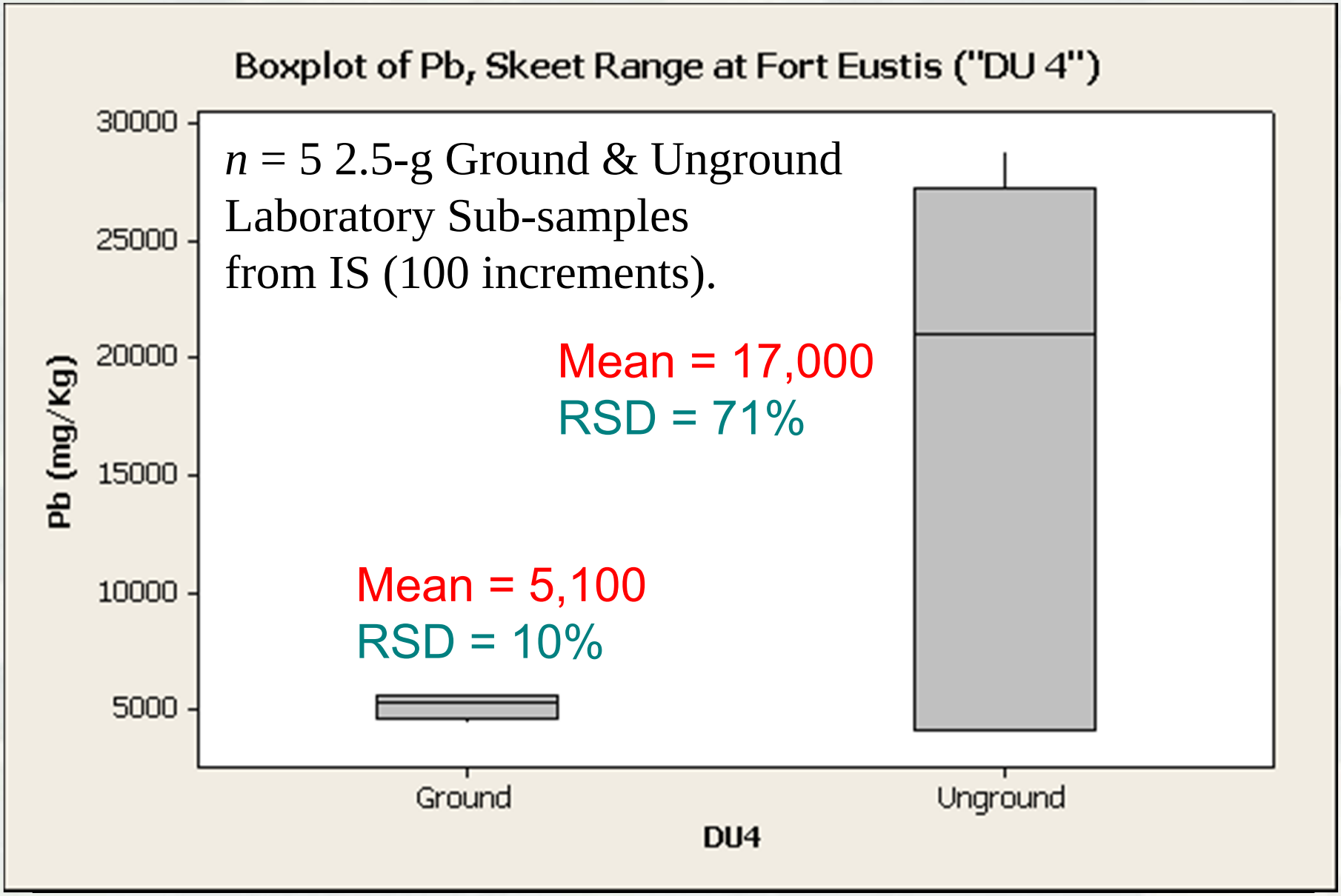


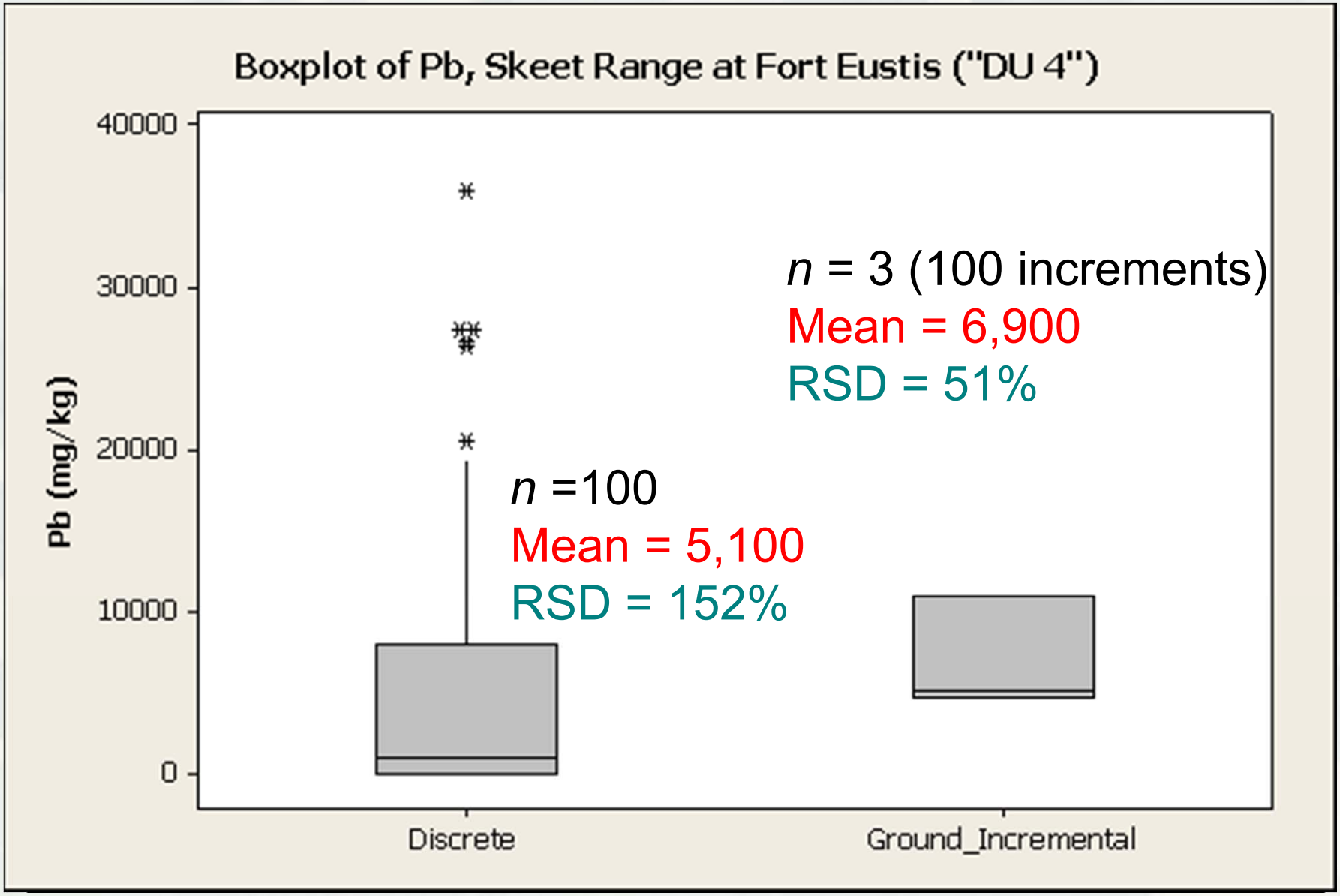
Method Blanks (Ground Glass)



Ground vs. Unground IS Field Replicates for Pb



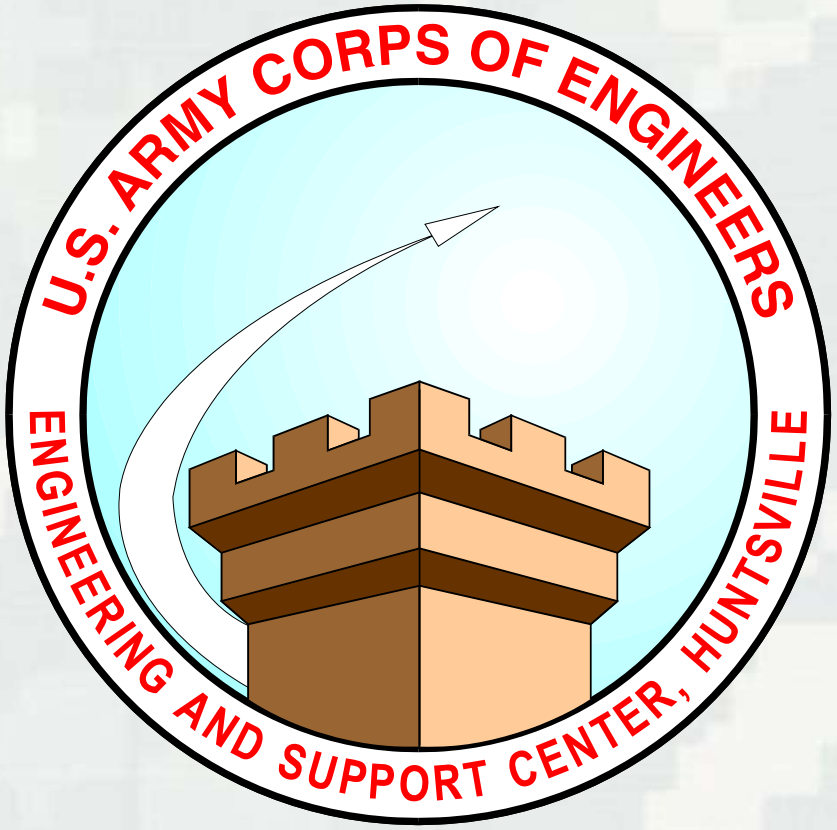

Boxplot of Pb, Skeet Range at Fort Eustis ("DU 4")
30000
25000
20000
15000
10000
5000
Pb (mg/Kg)
n = 5 2.5-g Ground & Unground
Laboratory Sub-samples
from IS (100 increments).
Mean = 17,000
RSD = 71%
Mean = 5,100
RSD = 10%
Ground
Unground
DU4


Boxplot of Pb, Skeet Range at Fort Eustis ("DU 4")
Pb (mg/kg)
40000
30000
20000
10000
0
Discrete
Ground_Incremental
n = 3 (100 increments)
Mean = 6,900
RSD = 51%
n =100
Mean = 5,100
RSD = 152%

Conclusions

- %RSD measures variability **not usability**.
  - ► Do not set arbitrary goals for %RSD. Use %RSD to qualitatively assess precision only.
  - ► Use 7-Step DQO Process to develop sampling design and evaluate usability.
- Large number of increments of limited value if lab sub-sampling variability is large (because soils with metal particles are not ground).
- Even IS approach with grinding may not be adequate if *n* is small.

Questions?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